de ces deux schémas ne nous a permis d'interpréter correctement les valeurs des F_o. Ce fait nous a conduit à penser que le site 8(*b*) n'est pas un puits de potentiel pour le thallium.

L'occupation de positions 32(*e*) par le thallium nous avait été suggérée par des calculs de potentiel électrostatique qui incluaient le terme d'origine dipolaire, ici très important compte tenu de la grande polarisabilité du thallium (Fourquet, 1977). La détermination structurale précise et confirme donc cette hypothèse; elle permet en outre de corréler entre elles d'autres observations sur $TlNb_2O_5F$: à la température ambiante l'existence d'une bande de relaxation dipolaire diélectrique (Fourquet, 1977) ainsi que le rétrécissement très sensible de la largeur de raie du signal RMN du thallium en fonction de la température (Sleight, Gulley & Berzins, 1977). Ces deux derniers résultats trouvent leur interprétation dans un mouvement des ions thallium dans leurs cages; ceux-ci passeraient d'un type de position 32(*e*) à un autre avec un temps de relaxation de l'ordre de 10^{-5} s. Cette mobilité est en relation étroite avec le phénomène de conduction ionique par le thallium observé sur $TlNb_2O_5F$ par Fourquet (1977) et Sleight, Gulley & Berzins (1977).

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Comparison of the Crystal Structures of Alkaline (M = Li, Na, K, Rb, Cs) and Pseudo-Alkaline (M = NO, NH_4) Tetrachloroaluminates, MAlCl$_4$

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Abstract

In the MAlCl$_4$ family, the salts of voluminous cations (NO, NH_4, Rb) and CsAlCl$_4$ have the $BaSO_4$ barytes-type structure (space group *Pnma*). It is possible to describe the KAlCl$_4$ (space group $P2_1$) and the NaAlCl$_4$ (space group $P2_12_12_1$) structures as deformations of this basic structure; the LiAlCl$_4$ structure (space group $P2_1/c$) is built up from LiCl$_6$ octahedra layers linked together by AlCl$_4$ tetrahedra. The mean Al—Cl lengths, corrected for thermal-motion effects, range from 2·141 Å (NOAlCl$_4$) to 2·150 Å (NH_4AlCl$_4$).

Introduction

Solid-state structural data related to complex $A^{I}M^{III}$Cl$_4$ ternary chlorides are not very numerous and always

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partial. Thus, for example, in the tetrachloroaluminate-family salts, the only structures that were known previously are those of the Na (Baenziger, 1951) and Cs (Gearhart, 1972) salts. This is probably due to the hygroscopicity of these salts which makes it difficult to prepare and handle them. Nevertheless, this structural family is important because $NaFeCl_4$ was proved to be isomorphous with $NaAlCl_4$ (Richards & Gregory, 1965), $CsFeCl_4$ with $CsAlCl_4$ (Meyer, 1977) and $CsGaCl_4$ with $CsAlCl_4$ (Gearhart, Beck & Wood, 1975). Furthermore, these compounds have important practical applications, particularly as catalysts and electrolytes in the molten state.

The use of the inorganic solvents SO_2 and $SOCl_2$ (Barbier & Mairesse, 1971) enabled us to prepare single crystals of all the alkaline and pseudo-alkaline salts. These crystals were studied by X-ray diffraction and Raman scattering (Mairesse, 1978). We have previously reported the crystal structures of $NOAlCl_4$ (Barbier, Mairesse, Wignacourt & Baert, 1976), $LiAlCl_4$ (Mairesse, Barbier, Wignacourt & Baert, 1977), NH_4AlCl_4 (Mairesse, Barbier, Wignacourt, Rubbens & Wallart, 1978) and $KAlCl_4$ (Mairesse, Barbier & Wignacourt, 1978). The present paper reports the refinements of the $CsAlCl_4$ and $NaAlCl_4$ crystal structures together with a comparative study of all members of this salt family.

Refinements of the Cs and $NaAlCl_4$ crystal structures

$CsAlCl_4$

The $CsAlCl_4$ crystal structure has already been described (Gearhart, 1972) but, in fact, the determination was carried out from the isomorphous compound $CsGaCl_4$, with intensities collected by precession photographs with Cu $K\alpha$ radiation and without an absorption correction: this explains the inaccuracy of this refinement ($R = 0{\cdot}126$ with 399 observed reflexions).

The crystal selected for the data collection was coated with dried paraffin and mounted in a sealed quartz capillary, as were the other single crystals of this family. It was a parallelepiped with a rhombic base; the boundary faces, defined by the forms $\pm\{210\}$, $\pm\{2\bar{1}0\}$ and $\pm\{001\}$, had the dimensions $0{\cdot}26 \times 0{\cdot}26 \times 0{\cdot}36$ mm. The structural parameters, lattice energy (Jenkins, Pratt, Mairesse, Barbier & Wignacourt, 1979) and data-collection conditions are summarized in Table 1, together with those of the other salts. Since $CsAlCl_4$ is the most absorbing of the alkaline salts (except for Rb) for Mo $K\alpha$ radiation, the good quality of the crystal and the simplicity of its shape enabled us to check the influence of absorption in the alkaline tetrachloroaluminates. The refinement was carried out with, on the one hand, non-corrected and, on the other, corrected intensities ($\mu = 6{\cdot}2$ mm^{-1}). In the first case we obtained $R = 0{\cdot}046$ and $R_w = 0{\cdot}065$ [$w = 1/\sigma^2(F)$] without taking into account anomalous-dispersion effects. When an absorption correction was applied (Alcock, 1969), with the same weighting scheme and including the imaginary component of dispersion (Cromer & Liberman, 1970), we obtained $R = 0{\cdot}047$ and $R_w = 0{\cdot}060$. In both refinements, the observed Al—Cl lengths

Table 2. $CsAlCl_4$: *positional parameters* ($\times 10^5$) *with their e.s.d.'s*

	x	y	z
Al	57016 (19)	25000	69293 (23)
Cl(1)	71186 (26)	25000	55165 (27)
Cl(2)	40999 (29)	25000	58962 (46)
Cl(3)	58375 (13)	915 (22)	82699 (15)
Cs^+	68056 (4)	25000	16536 (6)

Table 1. *Crystallographic parameters (room-temperature), lattice energy and data-collection conditions for the alkaline and pseudo-alkaline tetrachloroaluminates (Philips PW* 1100 *computer-controlled four-circle diffractometer with graphite-monochromatized* Mo $K\alpha$ *radiation, ω–θ scan technique)*

	Li^+	Na^+	K^+	Cs^+	NO^+	NH_4^+
a (Å)	7·007 (3)	9·886 (3)	10·481 (9)	11·641 (8)	10·411 (8)	11·022 (6)
b (Å)	6·504 (4)	6·167 (2)	7·183 (5)	7·116 (5)	7·055 (3)	7·072 (3)
c (Å)	12·995 (10)	10·322 (3)	9·273 (5)	9·373 (7)	9·461 (5)	9·257 (5)
	$\beta = 93{\cdot}32$ (5)°		$\alpha = 93{\cdot}10$ (3)°			
V (Å^3)	591	629	697	776	695	722
Z	4	4	4	4	4	4
D_c (Mg m^{-3})	1·98	2·03	1·98	2·58	1·90	1·72
Lattice energy (kJ mol^{-1})	567	546	519	505		522
Space group	$P2_1/c$	$P2_12_12_1$	$P2_1$	$Pnma$	$Pnma$	$Pnma$
μ (mm^{-1})	2·0	1·9	2·2	6·2	1·6	1·6
Crystal size (mm)	~0·35 × 0·30 × 0·30	~0·25 × 0·25 × 0·30	~0·30 × 0·25 × 0·25	0·26 × 0·26 × 0·36	~0·20 × 0·30 × 0·70	~0·25 × 0·35 × 0·20
Scan range (°)	$6 \le 2\theta \le 62$ (hkl, $hk\bar{l}$, $\bar{h}\bar{k}l$, $\bar{h}kl$)	$6 \le 2\theta \le 60$ (hkl)	$6 \le 2\theta \le 60$ (hkl, $\bar{h}kl$)	$6 \le 2\theta \le 60$ (hkl)	$6 \le 2\theta \le 60$ (hkl)	$5 \le 2\theta \le 60$ (hkl, $\bar{h}kl$)
Scan width (°)	1·0	1·50 + tan θ	1·60	1·20	1·25	0·90 + 0·4 tan θ
Scanning speed (° s^{-1})	0·04	0·0205	0·03	0·03	0·05	0·033
Number of reflexions used	1434 ($I > 2\sigma I$)	1240 ($I > 2\sigma I$)	1501 ($I > 3\sigma I$)	929 ($I > 2\sigma I$)	586 ($I > 3\sigma I$)	596 ($I > 2\sigma I$)
Absorption corrections	No	No	No	Yes	No	No
Final R	0·029	0·025	0·035	0·047	0·042	0·053
Final R_w	0·035	0·039	0·046	0·060		0·069

are identical, the differences being less than the e.s.d.'s. Hence, absorption barely alters the structural parameters of this salt and the same must hold true for the others (in which these effects could not be taken into account). The results reported here are those of the second refinement: atomic coordinates in Table 2, intra-anionic bond lengths and angles in Table 3 and the cation environment in Table 4.* The ionic packing is similar to that in the isomorphous NH_4AlCl_4 ($BaSO_4$ barytes-type structure). The shortest $Cs^+\cdots Cl$ distance is 3·584 (4) Å, which is close to that in CsCl (3·560 Å, Wells, 1975). If we take into account all the $Cs\cdots Cl$ lengths which are less than the shortest $Cs\cdots Al$ distance, the Cs^+ cation is surrounded by 12 Cl atoms. But we have to point out the dissymmetry of the anionic environment: although each Cl atom interacts with three Cs^+ cations, Cl(2) is different from the others, since it is surrounded both by the nearest cation [3·584 (4) Å] and by two more distant ones [4·364 (4) Å] (Table 4). Therefore, these two cations have a weaker influence, which must explain the greater thermal motion of Cl(2): $B_{eq} = 9{\cdot}20$ Å^2 instead of 5 Å^2 (mean value) for the others. The same phenomenon is observed in the NH_4^+ salt in which the cation, in the temperature range studied (298–10 K), behaves like a spherical ion without any apparent restricting motion (Mairesse, Barbier, Wignacourt, Rubbens & Wallart, 1978).

For the Rb^+ salt, we did not manage to obtain single crystals suitable for a complete structural determination but, from the systematic extinctions and the Raman scattering spectra (Rubbens, Wallart, Barbier, Mairesse & Wignacourt, 1978), it is clear that it is isostructural with the Cs^+ salt. The cell parameters determined on a computer-controlled diffractometer are $a = 11{\cdot}136$ (10), $b = 7{\cdot}084$ (6), $c = 9{\cdot}258$ (9) Å.

* Lists of structure factors (for the Cs, Na, Li and NO salts) and anisotropic thermal parameters (for the Cs and Na salts) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34371 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. $CsAlCl_4$: *intra-anionic distances* (Å) *and angles* (°) *with their e.s.d.'s*

Cl(3′) is related to Cl(3) by the mirror at $y = \frac{1}{4}$.

Al–Cl(1)	2·115 (4)	Cl(1)–Cl(2)	3·532 (4)
Al–Cl(2)	2·101 (4)	2 × Cl(1)–Cl(3)	3·438 (3)
Al–Cl(3)	2·131 (2)	2 × Cl(2)–Cl(3)	3·461 (4)
		Cl(3)–Cl(3′)	3·428 (2)

Cl(1)–Al–Cl(2)	113·80 (13)
2 × Cl(1)–Al–Cl(3)	108·13 (11)
2 × Cl(2)–Al–Cl(3)	109·73 (12)
Cl(3)–Al–Cl(3′)	107·08 (10)

Table 4. *Coordination about the* Cs^+ *cation* (Å)

Coding of equivalent positions: (1) x,y,z; (2) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$; (3) $\bar{x}, \frac{1}{2} + y, \bar{z}$; (4) $\frac{1}{2} + x, y, \frac{1}{2} - z$. Cs^+ is in position (1), Cl(3) 3/101 means that Cl(3) is in position (3) translated by $1a,0b,1c$.

Cl(2) 4/000	3·584 (4)	Cl(3) 1/00$\bar{1}$	3·777 (1)
Cl(3) 3/101	3·588 (2)	Cl(3′) 1/00$\bar{1}$	3·777 (1)
Cl(3′) 3/1$\bar{1}$1	3·588 (2)	Cl(1) 2/10$\bar{1}$	3·920 (1)
Cl(3) 2/10$\bar{1}$	3·636 (2)	Cl(1) 2/1$\bar{1}\bar{1}$	3·920 (1)
Cl(3′) 2/1$\bar{1}\bar{1}$	3·636 (2)	Cl(2) 3/101	4·364 (4)
Cl(1) 1/000	3·639 (3)	Cl(2) 3/1$\bar{1}$1	4·364 (4)

$NaAlCl_4$

The structure of this compound is known (Baenziger, 1951) and has been refined (Scheinert & Weiss, 1976) from NMR and NQR studies of a single crystal. The results of our refinement (for conditions see Table 1) are reported in Tables 5, 6 and 7 with a different description of the structure to make the comparison with those of other alkaline salts easier.

Table 5. $NaAlCl_4$: *positional parameters* ($\times 10^5$) *with their e.s.d.'s*

	x	y	z
Al	51429 (6)	20707 (9)	96226 (6)
Cl(1)	68550 (5)	10957 (9)	85152 (5)
Cl(2)	33503 (5)	7337 (9)	87726 (5)
Cl(3)	52257 (6)	7458 (9)	115367 (5)
Cl(4)	50874 (6)	55281 (8)	96786 (6)
Na^+	71343 (12)	31122 (23)	37466 (15)

Table 6. $NaAlCl_4$: *intraionic distances* (Å) *and angles* (°) *with their e.s.d.'s*

Al–Cl(1)	2·129 (1)	Cl(1)–Cl(2)	3·482 (1)
Al–Cl(2)	2·142 (1)	Cl(1)–Cl(3)	3·517 (1)
Al–Cl(3)	2·140 (1)	Cl(1)–Cl(4)	3·459 (1)
Al–Cl(4)	2·134 (1)	Cl(2)–Cl(3)	3·403 (1)
		Cl(2)–Cl(4)	3·545 (1)
		Cl(3)–Cl(4)	3·521 (1)

Cl(1)–Al–Cl(2)	109·21 (3)	Cl(2)–Al–Cl(3)	105·24 (3)
Cl(1)–Al–Cl(3)	110·95 (3)	Cl(2)–Al–Cl(4)	111·99 (3)
Cl(1)–Al–Cl(4)	108·49 (3)	Cl(3)–Al–Cl(4)	110·95 (3)

Table 7. *Coordination about the* Na^+ *cation* (Å)

Coding of equivalent positions: (1) x,y,z; (2) $\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$; (3) $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$; (4) $\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}$.

Cl(1) 2/10$\bar{1}$	2·791 (2)	Cl(2) 3/101	3·066 (2)
Cl(3) 3/101	2·859 (2)	Cl(4) 3/1$\bar{1}$1	3·164 (2)
Cl(2) 4/001	2·951 (2)	Cl(3) 1/00$\bar{1}$	3·301 (2)
Cl(4) 2/11$\bar{1}$	3·028 (2)	Cl(1) 2/11$\bar{1}$	3·717 (2)

Comparison of the structures

Ionic packing

All the unit cells are characterized by the same multiplicity ($Z = 4$) but show considerable diversity of spatial arrangement. In contrast to other tetrahedral anion salts such as MBF$_4$ (Clark & Lynton, 1969; Brunton, 1969) and MClO$_4$ (Johansson & Lindqvist, 1977; Choi, Prask & Prince, 1976), the K$^+$ salt does not crystallize in the same space group as the Rb$^+$, Cs$^+$ and NH$_4^+$ salts (Table 1). The KAlCl$_4$ lattice symmetry of $P2_1$ is close to $P2_1/m$ (Mairesse, Barbier & Wignacourt, 1978) but, as can be seen from its Raman spectrum (Rubbens, Barbier, Mairesse, Wallart & Wignacourt, 1977), the crystal behaves like an apparent orthorhombic crystal in $P2_12_12_1$, the space group of NaAlCl$_4$. Thus it should be possible to understand the structural filiation of all these salts from Cs$^+$ to Na$^+$. The comparison of the projections obtained after various combinations of axes permutations enabled us to determine this filiation. From NaAlCl$_4$ in the orientation used by Baenziger for space group $P2_12_12_1$ with parameters (subscripts 1) $a_1 > b_1 > c_1$, we have permuted the axes such that (subscripts 2) $a_2 = b_1$, $b_2 = c_1$ and $c_2 = a_1$. The atomic coordinates are therefore transformed in such a way that $x_2 = -y_1, y_2 = z_1$ and $z_2 = -x_1$ (enantiomorphs changed). Furthermore, to obtain a homogeneous atomic-numbering scheme, we have modified the numbering as follows: Cl(4)$_2$ ≡ Cl(1)$_1$, Cl(1)$_2$ ≡ Cl(2)$_1$, Cl(3)$_2$ ≡ Cl(3)$_1$ and Cl(2)$_2$ ≡ Cl(4)$_1$. Finally, we have transformed the atomic coordinates of the Na$^+$ cation, applying the symmetry operation $\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$ of space group $P2_12_12_1$. All these transformations lead to a new description of the NaAlCl$_4$ crystal structure in which the Al—Cl(4) bond is nearly parallel to **b**, according to the values given in Tables 5, 6 and 7.

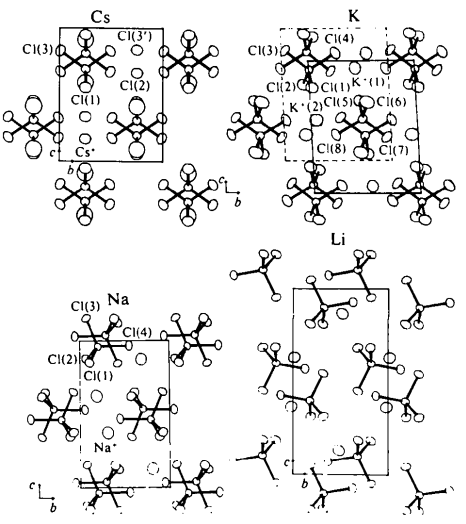

Fig. 1. Projections down **a** illustrating the arrangements of the M^+ and AlCl$_4^-$ ions in the CsAlCl$_4$, KAlCl$_4$, NaAlCl$_4$ and LiAlCl$_4$ unit cells. (For K$^+$ the dotted lines refer to the $P2_1/m$ pseudo cell.)

The Cs$^+$, K$^+$ and Na$^+$ crystal structure projections down **a** (Fig. 1) enable us to visualize the filiation easily. In the NaAlCl$_4$ unit cell, the main deformation, compared with the K$^+$ and Cs$^+$ unit cells, is a rotation of about 35° of the anionic group around an axis parallel to **a** through the Al atom. In spite of the modifications resulting from the cation change, the packing mode and the relative anion–cation disposition remain very similar and all these structures, from CsAlCl$_4$ to NaAlCl$_4$, can therefore be described from deformations of the barytes basic structure type.

For LiAlCl$_4$ the deformations are much more important, as can be seen from the unit-cell parameters (Table 1). Nevertheless, some resemblance to NaAlCl$_4$ (concerning the anionic tetrahedra orientations) is visible in Fig. 1.

Anion–cation environment and packing density

These structural modifications result from the different sizes of the cations and imply coordination variations. Except for LiAlCl$_4$, this coordination is difficult to define owing to the spread of the $M^+\cdots$Cl distances, while the shortest $M^+\cdots$Cl value is always very close to that in the corresponding alkaline chlorides MCl. We have taken into account all the $M^+\cdots$Cl distances less than the shortest $M^+\cdots$Al because the partial charge of the Al atom has been evaluated as +0·32 [$q_{Cl} = -0{\cdot}38$ (7)], according to lattice-energy calculations (Jenkins *et al.*, 1979). We thus obtain coordination numbers of 8 for Na$^+$, 9 for K$^+$ and 12 for NH$_4^+$ and Cs$^+$, the coordination polyhedra having no characteristic geometric shape. In LiAlCl$_4$, the Li$^+$ cation is octahedrally surrounded by Cl atoms as in Co(AlCl$_4$)$_2$ (Ibers, 1962). Thus we can describe this structure as being built up from AlCl$_4$

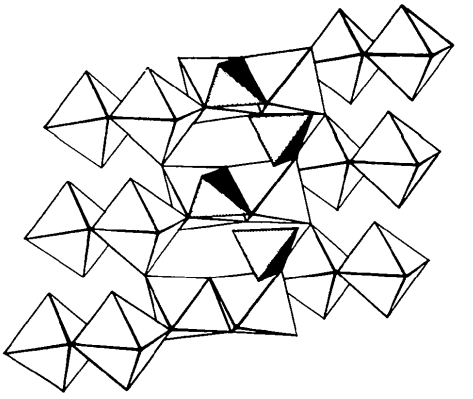

Fig. 2. Linking of LiCl$_6$ octahedra and AlCl$_4$ tetrahedra in LiAlCl$_4$. For reasons of clarity only a few tetrahedra have been drawn.

tetrahedra and $LiCl_6$ octahedra (both distorted). The octahedra are linked in pairs by sharing an edge, and each pair is linked to four other pairs by sharing one corner. All these octahedra roughly form a layer parallel to the *ac* plane, and these layers are linked together by the $AlCl_4$ tetrahedra. Each tetrahedron shares two edges with one octahedron pair and two corners with two other octahedra (Fig. 2).

We have calculated the packing densities of the different structures, using Bondi's (1964) method to calculate the van der Waals volume of the $AlCl_4^-$ anion. For this purpose the estimated values were as follows. For the Al—Cl length we used 2·15 Å, corresponding to the average value corrected for thermal-motion effects. For the Cl atom we used the van der Waals radius $r = 1{\cdot}75$ Å evaluated by Bondi. In fact, in the most symmetric structures (space group *Pnma*), the crystallographic sites of the anions are mirrors $y = \frac{1}{4}$ and $y = \frac{3}{4}$, and the coordinates of the Cl atoms out of the mirrors [Cl(3) and Cl(3′)] are nearly $y = 0$ and $y = \frac{1}{2}$. The *b* parameter of these unit cells therefore corresponds to $4r_{Cl} \simeq 7$ Å (7·055 Å in $NOAlCl_4$; Barbier, Mairesse, Wignacourt & Baert, 1976), which justifies the r_{Cl} value. We thus obtain an $AlCl_4$ tetrahedron built up from four close-packed hard equal spheres. The Al radius r_{Al} chosen was 1·25 Å, which corresponds to an atom occupying all the space left in the tetrahedron. This value is similar to that proposed for the Al tetrahedral covalent radius: 1·23 Å (Van Vechten & Phillips, 1970). The van der Waals volume of one tetrahedron is then calculated to be 116·5 Å^3, and therefore 466 Å^3 for the four groups in the different unit cells. The $M^+\cdots$Cl distances vary widely within the same cationic coordination pattern so it seemed physically more sound to use, in each case, the shortest observed distance $d(M^+\cdots Cl)$ to estimate the alkaline-cation ionic radius r^+_{est}. Therefore, these values are generally slightly weaker than Shannon's (1976) effective ionic radii IR, which are mean values. Nevertheless, when we take into consideration the whole coordination polyhedron, we obtain a mean cationic radius $\langle r^+\rangle$ very close to Shannon's crystal radius CR (Table 8) (in Cs^+ and NH_4^+ we have only taken into account the ten nearest Cl atoms, the other two being clearly more distant). The packing-density values so obtained are nearly identical in the Cs^+, NH_4^+ and K^+ salts, while in

Table 8. *Compactnesses of the different* $MAlCl_4$ *crystal structures*

CN: coordination number. CR: crystal radius and IR: effective ionic radius, both from Shannon (1976).

	CR	IR	r^+_{est}	$\langle r^+\rangle$	V_{cell}	V_{calc}	τ
Li^+(CN 6)	0·90 Å	0·76 Å	0·70$_5$ Å	0·90 Å	591 Å^3	472 Å^3	0·80
Na^+(CN 8)	1·32	1·18	1·04	1·35	629	485	0·77
K^+(CN 9)	1·69	1·55	1·45	1·67	697	517	0·74
NH_4^+(CN 10)	not tabulated		1·58	1·85	722	532	0·74
Cs^+(CN 10)	1·95	1·81	1·83$_5$	1·95	776	570	0·73

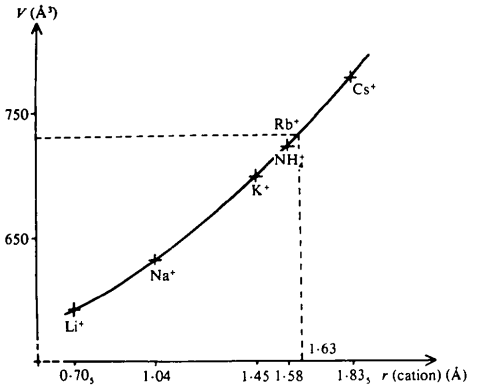

Fig. 3. A plot of the volumes of the different unit cells *vs* the ionic radii (estimated from the shortest $M^+\cdots$Cl distance).

Na^+ the packing density is between that of the above-mentioned group and that of the Li^+ (which is a maximum). By plotting the unit-cell volumes *V versus* the cationic radii r^+_{est}, we obtain a regular curve (Fig. 3) which enables us to estimate the Rb^+ radius in $RbAlCl_4$ as 1·63 Å [CR = 1·80 Å and IR = 1·66 Å for coordination number (CN) = 10; Shannon, 1976].

Comparison of the Al—Cl lengths

A survey of the mean distances $\langle d(Al—Cl)\rangle$ resulting from least-squares refinements (observed distances) would seem to indicate a decrease of $\langle d(Al—Cl)\rangle$ when the counterion size increases. But these decreasing observed distances are on a par with the increasing thermal motions of the atoms. Therefore, we have corrected the Al—Cl lengths for thermal-motion effects (Busing & Levy, 1964). Initially, we checked the rigid-body model with the **TLS** analysis (Schomaker & Trueblood, 1968) (Table 9). We obtained the closest fit with the Na^+ and Li^+ salts. For the other salts, the fit is a little poorer. Comparison of the **TLS** results with the Al—Cl bond directions does not show any correlation between the bond direction cosines and the principal axes of libration. Thus no Al—Cl bond plays a dominant part and consequently no particular $Cl\cdots M^+$ interaction exists, which corroborates the ionic character of all these structures; this conclusion was also reached by Scheinert & Weiss (1976) in their NMR and NQR study of $NaAlCl_4$.

The $AlCl_4^-$ anion is also consistent with Busing & Levy's riding-motion model, as the thermal motion of the Al atom (centre of mass of the tetrahedral anion) is always lower than that of the Cl atoms. In Table 10 are reported the observed Al—Cl lengths, the upper and lower bounds (as defined by Busing & Levy) which are independent of the joint distribution describing the correlated motion of the atoms involved, and the

Table 9. *Rigid-body-motion parameters of the* $AlCl_4^-$ *anions in each salt*

The tensors (with their e.s.d.'s) are referred to a Cartesian coordinate system defined by X parallel to **a**, Y parallel to $\mathbf{c}^* \wedge \mathbf{a}$, and Z parallel to $\mathbf{c}^*$. The origin is at the centre of mass. The trace of **S** has been set = 0.

		T ($\times 10^4$) (Å^2)			**L** ($\times 10^4$) (rad^2)		**S** ($\times 10^4$) (Å rad)		
$LiAlCl_4$	238 (7)	−27 (7)	−10 (6)	44 (5)	−2 (5)	21 (3)	6 (7)	11 (4)	−1 (3)
		311 (7)	−7 (7)		35 (3)	8 (4)	2 (4)	−8 (6)	0 (3)
			263 (8)			31 (5)	−7 (3)	−9 (4)	2 (10)
		R.m.s. ΔU_{ij} = 0·0006 Å^2			E.s.d. U_{ij} = 0·0010 Å^2				
$NaAlCl_4$	315 (8)	15 (10)	1 (8)	45 (4)	5 (7)	−2 (5)	13 (8)	11 (5)	−2 (4)
		235 (7)	5 (9)		40 (3)	4 (6)	5 (5)	−11 (5)	−6 (5)
			287 (8)			40 (5)	4 (3)	−2 (5)	−2 (11)
		R.m.s. ΔU_{ij} = 0·0007 Å^2			E.s.d. U_{ij} = 0·0011 Å^2				
$KAl(1)Cl_4$	434 (30)	−33 (40)	49 (21)	109 (16)	14 (30)	5 (7)	11 (41)	20 (17)	7 (8)
		348 (30)	40 (21)		82 (18)	31 (7)	−24 (16)	8 (39)	4 (8)
			317 (39)			39 (25)	−38 (9)	3 (9)	−19 (42)
		R.m.s. ΔU_{ij} = 0·0024 Å^2			E.s.d. U_{ij} = 0·0042 Å^2				
$KAl(2)Cl_4$	336 (29)	27 (38)	−23 (20)	86 (16)	−12 (29)	−20 (7)	−30 (38)	0 (16)	−7 (7)
		343 (28)	32 (20)		100 (17)	35 (7)	84 (16)	17 (38)	−31 (8)
			373 (37)			105 (24)	54 (6)	37 (9)	13 (40)
		R.m.s. ΔU_{ij} = 0·0023 Å^2			E.s.d. U_{ij} = 0·0040 Å^2				
$CsAlCl_4$	370 (26)	0 (39)	−55 (20)	91 (14)	0 (30)	−24 (8)	0 (38)	47 (17)	0 (8)
		428 (27)	0 (20)		180 (14)	0 (7)	−117 (16)	0 (38)	87 (7)
			367 (36)			101 (23)	0 (9)	−54 (9)	0 (39)
		R.m.s. ΔU_{ij} = 0·0023 Å^2			E.s.d. U_{ij} = 0·0039 Å^2				
NH_4AlCl_4	351 (26)	0 (38)	−13 (19)	151 (14)	0 (29)	−30 (7)	0 (38)	36 (16)	0 (8)
		419 (26)	0 (19)		167 (13)	0 (7)	−120 (16)	0 (37)	36 (7)
			338 (35)			148 (23)	0 (9)	−40 (8)	0 (38)
		R.m.s. ΔU_{ij} = 0·0022 Å^2			E.s.d. U_{ij} = 0·0038 Å^2				
$NOAlCl_4$	359 (23)	0 (34)	8 (17)	118 (12)	0 (26)	−17 (6)	0 (33)	36 (14)	0 (6)
		436 (23)	0 (17)		104 (12)	0 (6)	−58 (14)	0 (33)	3 (6)
			441 (31)			102 (21)	0 (7)	2 (7)	0 (34)
		R.m.s. ΔU_{ij} = 0·0020 Å^2			E.s.d. U_{ij} = 0·0034 Å^2				

corrected bond lengths obtained from both the rigid-body and the riding-motion models. Each corrected distance is within the range so defined, whatever the chosen approach may be. Both models are therefore suitable. Because of the tetrahedral symmetry of the $AlCl_4^-$ anion, we can point out that, in the rigid-body model, all the bond lengths are affected by the same corrective term. This model is the most convenient for the Li^+ and Na^+ salts, as shown previously (Table 9). Besides, in these structures, the Cl thermal-motion coefficients have a similar order of magnitude. The same does not hold true for the other salts, the spread being much greater, especially in NH_4AlCl_4 and $CsAlCl_4$ [Cl(2) atom]. Consequently it seems more advisable to retain the second model (riding motion) for the K^+, NO^+, NH_4^+ and Cs^+ salts. Thus we notice that the bond-length average values range, in this whole family, from 2·141 Å ($NOAlCl_4$) to 2·150 Å (NH_4AlCl_4), while the same uncorrected distances range from $2{\cdot}117_5$ to $2{\cdot}137_5$ Å. Then the corrections applied lead to almost the same $\langle d(\text{Al—Cl})\rangle$ value and also tend to equalize the bond lengths in each anion (except for the Li^+ and Na^+ salts). Furthermore, it is useful to recall that the nature of the crystals studied has prevented us from applying absorption corrections in most cases (the Cs^+ salt being the exception). It is known that neglect of absorption correction primarily affects the thermal-motion parameters (Kratky & Dunitz, 1975; Murray-Rust & Murray-Rust, 1975; Payan & Haser, 1976), which values are used for correcting interatomic distances. Moreover, even in the Cs^+ salt, for which the absorption effects were taken into account, the thermal motion is so important [Cl(2) 9 Å^2] that it must be the validity limit of the approximations: the conventional quadratic ones used to define thermal motion, as well as those used to evaluate the Busing & Levy corrections. It seems probable that the results obtained with low-temperature data would be even more similar, at least for the most voluminous cations.

It may seem paradoxical, at first sight, that in this ionic compound family, the atomic thermal motion

Table 10. *Observed and corrected* Al—Cl *distances* (Å) *in the* $MAlCl_4$ *salts*

Mean values are in angle brackets.

	Observed Al—Cl (in the order 1–2–3–4)		Bounds Lower	Bounds Upper	Corrected values: Rigid-body motion		Corrected values: Riding motion	
$LiAlCl_4$	2·127 (1)		2·128	2·195	2·139		2·136	
	2·146 (1)	$\langle 2{\cdot}137_5 \rangle$	2·147	2·209	2·158	$\langle 2{\cdot}149_5 \rangle$	2·153	$\langle 2{\cdot}145 \rangle$
	2·154 (1)		2·155	2·220	2·166		2·162	
	2·123 (1)		2·124	2·192	2·135		2·130	
$NaAlCl_4$	2·129 (1)		2·130	2·198	2·142		2·138	
	2·142 (1)	$\langle 2{\cdot}136 \rangle$	2·143	2·208	2·155	$\langle 2{\cdot}149 \rangle$	2·150	$\langle 2{\cdot}145 \rangle$
	2·140 (1)		2·141	2·210	2·153		2·149	
	2·134 (1)		2·135	2·207	2·147		2·142	
$KAl(1)Cl_4$	2·119 (5)		2·123	2·226	2·143		2·141	
	2·136 (4)	$\langle 2{\cdot}133_5 \rangle$	2·138	2·224	2·161	$\langle 2{\cdot}158 \rangle$	2·151	$\langle 2{\cdot}149_5 \rangle$
	2·139 (5)		2·141	2·240	2·164		2·152	
	2·140 (5)		2·142	2·239	2·164		2·154	
		$\langle 2{\cdot}129 \rangle$						$\langle 2{\cdot}147 \rangle$
$KAl(2)Cl_4$	2·137 (6)		2·140	2·238	2·168		2·154	
	2·115 (5)	$\langle 2{\cdot}124 \rangle$	2·124	2·239	2·146	$\langle 2{\cdot}155 \rangle$	2·148	$\langle 2{\cdot}145 \rangle$
	2·123 (5)		2·125	2·218	2·144		2·136	
	2·122 (5)		2·126	2·216	2·153		2·141	
$CsAlCl_4$	2·115 (4)		2·121	2·232	2·154		2·141	
	2·101 (4)	$\langle 2{\cdot}119_5 \rangle$	2·120	2·268	2·140	$\langle 2{\cdot}158_5 \rangle$	2·157	$\langle 2{\cdot}145_5 \rangle$
	2·131 (2) × 2		2·132	2·227	2·170		2·142	
NH_4AlCl_4	2·116 (2)		2·125	2·247	2·165		2·150	
	2·101 (3)	$\langle 2{\cdot}117_5 \rangle$	2·120	2·260	2·151	$\langle 2{\cdot}166_5 \rangle$	2·155	$\langle 2{\cdot}150 \rangle$
	2·126 (1) × 2		2·130	2·236	2·175		2·147	
$NOAlCl_4$	2·121 (3)		2·126	2·248	2·155		2·146	
	2·104 (3)	$\langle 2{\cdot}119 \rangle$	2·111	2·237	2·138	$\langle 2{\cdot}153 \rangle$	2·135	$\langle 2{\cdot}141 \rangle$
	2·125 (2) × 2		2·127	2·234	2·159		2·142	

should be higher when the cation is heavier. We believe it is because the cationic coordination polyhedra (except Li^+) are not very regular, the Cl atoms with a negative partial charge being linked in an $AlCl_4^-$ tetrahedron.

Thus the Al—Cl distances seem to be very similar, whatever the nature of the associated counterion may be. These results justify Scheinert & Weiss's observations about $NaAlCl_4$, and are consistent with those for other tetrachloroaluminates (Merryman, Edwards, Corbett & McCarley, 1974; Merryman, Corbett & Edwards, 1975). Their papers show, by ^{35}Cl NQR studies, that the spread in the different Cl atom nuclear quadrupole coupling constants was small; they attribute this to the small d(Al—Cl) variations. It is only for the Li^+ salt that the anionic distortion caused by the crystalline field can be noted; this is still rather weak but already significant (Mairesse *et al.*, 1977). This anionic distortion in the Li^+ salt was also observed in the molten salt by Raman scattering (Rytter & Øye, 1973). This $AlCl_4^-$ anion stability also appears in Raman spectra, the ν_s stretching frequency of the Al—Cl bond varying very little from 348 cm^{-1} for $NaAlCl_4$ to 356 cm^{-1} for Rb and NH_4AlCl_4 at room temperature (Barbier, Mairesse, Wignacourt, Wallart & Rubbens, 1976).

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Structure Cristalline du Sulfate Acide d'Indium(III) Hydraté

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Abstract

The compound is orthorhombic. The unit cell, with $a = 9{\cdot}997$ (3), $b = 5{\cdot}477$ (2), $c = 18{\cdot}443$ (10) Å, contains four formula units, $d_m = 2{\cdot}48$; $d_x = 2{\cdot}50$ Mg m^{-3}; μ(Mo $K\alpha$) = 2·78 mm^{-1}. The crystal structure has been solved in space group *Pnam* from single-crystal data collected on an automated diffractometer by Patterson and Fourier syntheses and refined by least-squares methods. With anisotropic temperature factors, the final R value is 0·033 for 783 independent observed reflexions corrected for absorption effects. The crystal structure can be described in terms of layers perpendicular to the c axis consisting of indium atoms joined to four others by SO_4 groups. The coordination polyhedron around the indium atoms is completed by the water molecules forming an $InO_4(OH_2)_2$ distorted octahedron. These layers are linked together by oxonium ions. One $H_5O_2^+$ joins two sheets by the intermediary of short hydrogen bonds. In view of these results, the compound must be formulated as $(H_5O_2)^+[In(H_2O)_2(SO_4)_2]^-$ and named: diaquadisulfatoindic(III) acid dihydrate.This conclusion can be extended to acids $HM(SO_4)_2.4H_2O$ with M = Al, Ga, Tl, V, Fe and Ti.

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